

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 18-11-2013		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Sep-2008 - 31-Aug-2013	
4. TITLE AND SUBTITLE Development of Enabling Chemical Technologies for Power from Green Sources			5a. CONTRACT NUMBER W911NF-08-1-0412		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611104		
6. AUTHORS Sankaran Thayumanavan			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Massachusetts - Amherst Office of Grants and Contracts 70 Butterfield Terrace Amherst, MA 01003 -9242			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 54635-CH.20		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT The collaborative projects in this project at UMass Amherst involve two main thrusts: (i) Materials for photovoltaics applications; and (ii) Proton transport materials for fuel cell applications. Developing strategies for harnessing energy from renewable sources is a significant challenge facing the scientific community, due to the environmental, economic, and national security implications. Conversion of solar energy to electrical energy is one of the most promising approaches to addressing this issue. Nature provides both the source and the inspiration for a solution in the form of the sun and the photosynthetic apparatus, respectively. Similarly, nature also provides a rich					
15. SUBJECT TERMS organic photovoltaics, polymers, solar cells, fuel cells, proton exchange membranes					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Sankaran Thayumanavan
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 413-545-1313

Report Title

Development of Enabling Chemical Technologies for Power from Green Sources

ABSTRACT

The collaborative projects in this project at UMass Amherst involve two main thrusts: (i) Materials for photovoltaics applications; and (ii) Proton transport materials for fuel cell applications. Developing strategies for harnessing energy from renewable sources is a significant challenge facing the scientific community, due to the environmental, economic, and national security implications. Conversion of solar energy to electrical energy is one of the most promising approaches to addressing this issue. Nature provides both the source and the inspiration for a solution in the form of the sun and the photosynthetic apparatus, respectively. Similarly, nature also provides a rich array of materials that can be used as inspiration for proton exchange dynamics, which are critical for proton exchange membranes in fuel cells. We describe our efforts in these two main thrusts with this project.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
01/08/2013 15.00	Felicia A. Bokel, Ryan C. Hayward, Todd Emrick, Brenton A. G. Hammer. Cross-Linked Conjugated Polymer Fibrils: Robust Nanowires from Functional Polythiophene Diblock Copolymers, <i>Chemistry of Materials</i> , (09 2011): 4250. doi: 10.1021/cm2018345
01/08/2013 16.00	Bhooshan C. Popere, Andrea M. Della Pelle, Ambata Poe, Ganapathy Balaji, S. Thayumanavan. Predictably tuning the frontier molecular orbital energy levels of panchromatic low band gap BODIPY-based conjugated polymers, <i>Chemical Science</i> , (07 2012): 3093. doi: 10.1039/c2sc20731a
01/08/2013 19.00	Chikkannagari Nagamani, Jing Guo, S. Thayumanavan. Synthesis and characterization of phenol-based biaryl proton conducting polymers, <i>Journal of Polymer Science Part A: Polymer Chemistry</i> , (03 2012): 1187. doi: 10.1002/pola.25880
01/08/2013 18.00	Ganapathy Balaji, Andrea M. Della Pelle, Bhooshan C. Popere, A. Chandrasekaran, S. Thayumanavan. Synthesis and properties of thienopyrrole based heteroacenes – indolodibenzothienopyrrole and dicarbazolodithienopyrrole, <i>Organic & Biomolecular Chemistry</i> , (02 2012): 3455. doi: 10.1039/c2ob25087j
01/08/2013 17.00	Bhooshan C. Popere, Andrea M. Della Pelle, Ambata Poe, S. Thayumanavan. Macromolecular architectures for organic photovoltaics, <i>Physical Chemistry Chemical Physics</i> , (01 2012): 4043. doi: 10.1039/c2cp23422j
03/19/2009 1.00	Arpornrat Nantalaksakul†, Astrid Mueller, Akamol Klaikherd, Christopher J. Bardeen, S. Thayumanavan. Dendritic and Linear Macromolecular Architectures for Photovoltaics: A Photoinduced Charge Transfer Investigation, <i>Journal American Chemical Society</i> , (2009): . doi:
05/14/2009 2.00	Jiun-Tai Chen, Dian Chen, Thomas P. Russell. Fabrication of Hierarchical Structures by Wetting Porous Templates with Polymer Microspheres, <i>Langmuir</i> , (2009): . doi:
06/26/2012 14.00	Brandon L Greene, Crisjoe A Joseph, Michael James Maroney, R. Brian Dyer. Direct evidence of active site reduction and photo-driven catalysis in sensitized hydrogenase assemblies, <i>Journal of the American Chemical Society</i> , (06 2012): 0. doi: 10.1021/ja3042367
07/28/2010 4.00	Tejaswini S. Kale, K. Krishnamoorthy, Mukundan Thelakkat, and S. Thayumanavan. Charge Mobility in Nonconjugated Dendrons with Charge Transport Functionality in Every Layer, <i>Journal of Physical Chemistry Letters</i> , (01 2010): . doi:
07/28/2010 3.00	Arpornrat Nantalaksakul, Kothandam Krishnamoorthy, and S. Thayumanavan. Broadening Absorption in Conductive Polymers through Cross-linkable Side Chains in a Nonconjugated Polymer Backbone, <i>Macromolecules</i> , (01 2010): . doi:
09/20/2011 8.00	J. Matthew Chudomel, Paul M. Lahti, Joel T. Mague. 2-Bromo-1,3-bis[2-(2-naphthyl)vinyl]benzene benzene hemisolvate and 9-bromodinaphth[1,2-, <i>Acta Crystallographica Section C Crystal Structure Communications</i> , (12 2010): 43. doi: 10.1107/S0108270110052297

- 09/20/2011 12.00 Le Li, Caroline Miesch, P. K. Sudeep, Anna C. Balazs, Todd Emrick, Thomas P. Russell, Ryan C. Hayward. Kinetically Trapped Co-continuous Polymer Morphologies through Intraphase Gelation of Nanoparticles, Nano Letters, (05 2011): 1997. doi: 10.1021/nl200366z
- 09/20/2011 11.00 Lei Zhang, Sami M. Fakhouri, Feng Liu, Justin C. Timmons, Niva A. Ran, Alejandro L. Briseno. Chalcogenoarene semiconductors: new ideas from old materials, Journal of Materials Chemistry, (12 2010): 1329. doi: 10.1039/c0jm02522d
- 09/20/2011 10.00 Dipankar Basak, Scott Christensen, Sravan K. Surampudi, D. Venkataraman, Craig Versek, Daniel T. Toscano, Mark T. Tuominen, Ryan C. Hayward. Proton conduction in discotic mesogens, Chemical Communications, (04 2011): 5566. doi: 10.1039/c1cc10509d
- 09/20/2011 6.00 Chikkannagari Nagamani, Usha Viswanathan, Craig Versek, Mark T. Tuominen, Scott M. Auerbach, S. Thayumanavan. Importance of dynamic hydrogen bonds and reorientation barriers in proton transport, Chemical Communications, (05 2011): 6638. doi: 10.1039/c1cc11207d
- 09/20/2011 7.00 J. Matthew Chudomel, Boqian Yang, Michael D. Barnes, Marc Achermann, Joel T. Mague, Paul M. Lahti. Highly Twisted Triarylamine for Photoinduced Intramolecular Charge Transfer, The Journal of Physical Chemistry A, (08 2011): 8361. doi: 10.1021/jp203563y
- 09/22/2011 5.00 Felicia A. Bokel, Pallikkara K. Sudeep, Emily Pentzer, Todd Emrick, Ryan C. Hayward. Assembly of Poly (3-hexylthiophene)/CdSe Hybrid Nanowires by Cocrystallization, Macromolecules, (04 2011): 1768. doi: 10.1021/ma2003807

TOTAL: 17

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

7th Euroasian Meeting on Heterocyclic Chemistry, Istanbul, Turkey, "Heterocycles in Renewable Energy Materials" June 17-21, 2012

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

09/21/2011 13.00 Lynmarie K. Thompson. Solid-State NMR of MembraneProteins: Moving TowardsGreater Complexity,
Oxford, UK: Academic Press, Elsevier Linacre House, (05 2011)

TOTAL: 1

Patents Submitted

Patents Awarded

Awards

Award for Outstanding Research and Creativity, University of Massachusetts (2013)
International Advisory Board, Federation of Asian Polymer Societies (2012-13)
International Advisory Board, Polytech, India (2012)

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Andrea Della Pelle	0.98	
FTE Equivalent:	0.98	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ayyagari Venkata Subrahmanyam	0.07
FTE Equivalent:	0.07
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Annamalai Chandrasekaran	0.08	
FTE Equivalent:	0.08	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Andrea Della Pelle

Total Number:

1

Names of other research staff

NAME

Karen Hakala

FTE Equivalent:

Total Number:

PERCENT SUPPORTED

0.02

0.02

1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attached

Technology Transfer

FINAL REPORT

ARO Grant #W911NF-08-1-0412

“Development of Enabling Chemical Technologies for Power from Green Sources”

University of Massachusetts Amherst

The collaborative projects in this project at UMass Amherst involve two main thrusts: (i) Materials for photovoltaics applications; and (ii) Proton transport materials for fuel cell applications.

1. Materials for photovoltaics

Developing strategies for harnessing energy from renewable sources is a significant challenge facing the scientific community, due to the environmental, economic, and national security implications. Conversion of solar energy to electrical energy is one of the most promising approaches to addressing this issue. Nature provides both the source and the inspiration for a solution in the form of the sun and the photosynthetic apparatus, respectively. Although mimicking Nature's photosynthesis is a challenging task, it is feasible to design and synthesize materials towards efficient conversion of solar energy. One of the key issues in the design of materials for solar energy conversion is the relative placement of photoactive and electroactive functionalities to create charge-separated states. Note that the charges are created upon illumination of sunlight on photoactive molecules. We at UMass Amherst have developed various strategies to achieve materials that exhibit better charge separated states. Our approaches and discoveries obtained through ARO support are described in this report.

1.1. Dendrimers, which are branched macromolecules, provide a unique opportunity to accomplish this objective, since these molecules can be achieved with excellent control in the relative placement of functional groups. A photoinduced electron transfer process in a dendrimer having donors and acceptors placed at specific locations is shown in Figure 1. Although the architecture provides certain advantages over linear polymers, the dendrimer shown in Figure 1 does not seem ideal for ultimate use in photovoltaics. This is because the charge transfer process causes one of the charges to be localized at the core of the dendrimer. This location in a dendrimer is significantly encapsulated, and therefore opportunities for ultimately transporting this charge to an electrode are limited, if they exist at all. To circumvent the localization of charge at the core, Thayumanavan has designed and synthesized dendron-rod-coil architectures.

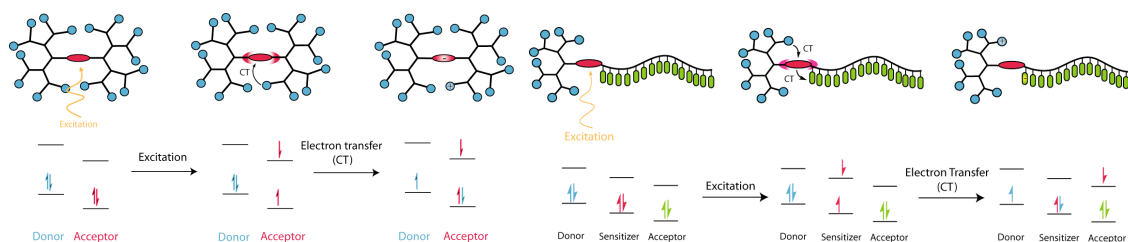


Figure 1. Cartoon showing electron transfer processes in dendritic and dendron-rod-coil backbone.

The molecules comprise an electron-donating triarylamine-based dendron, a photoactive thiophene-based core (rod) and naphthalenediimide-based electron-accepting coil.

The conclusions from the study are (i) the combination of the dendron and the polymer coil with a chromophore rod connecting the two is indeed advantageous for photoinduced charge transfer; (ii) dendron-rod-coil based triads exhibit higher efficiencies compared to either the dendron-rod or the rod-coil dyads; (iii) based on the efficiencies of the dyads, the dendrons and the polymer coil make similar contributions to the overall charge transfer-based quenching process; and, (iv) while all electron donor functionalities in the dendritic periphery can equally participate in the excited state quenching of the chromophore rod, the naphthalenediimide electron acceptor unit that is closest to the chromophore is the primary participant in the quenching that arises from the polymer coil.

1.2. We have previously explored the possibility of utilizing dendron-rod-coil polymers as the possible scaffolds for photoinduced charge separation. In this case, the rod component is the chromophore, while the dendron forms the hole transport component and the coil forms the electron transport component. While there have been several studies on charge transport through random coil polymer molecules, effect of dendritic architecture upon charge carrier mobility remains less understood. In the dendron-rod-coil architecture, it is essential that charges generated upon solar light excitation be separated through the dendritic architecture in the solid state. For this purpose, Thayumanavan has carried out a fundamental study that provides useful guidelines for incorporating charge transport functionalities in dendrimers and their utility in solid-state organic electronics. Hole-transporting triarylamine units were incorporated along the periphery of different generations of dendrimer containing insulating inner layers, and their field effect mobilities were measured. The charge mobility in these dendrimers was found to decrease with generation. We observed that increasing the density of charge transport units in the dendrimers, by incorporating triarylamines in every layer, improves the hole mobility in all generations. The mobility increases 4-fold from generation zero to one and drops and levels off at higher generations. These studies indicate that lower generation dendrimers with high density of charge transporting functionalities may prove to be good candidates for applications in organic photovoltaics. A combination of this understanding with the essential structural components to achieve photoinduced charge separation would unambiguously evaluate dendron-rod-coils as the possible scaffolds for achieving organized bulk heterojunction structures. Structure of the dendrons below and the trend in charge carrier mobilities are shown in Figure 2. The Figure also shows that when dendrons are fully decorated with charge transport moieties in every repeat unit, the charge carrier mobility is higher compared to the ones with only the peripheral charge transport units.

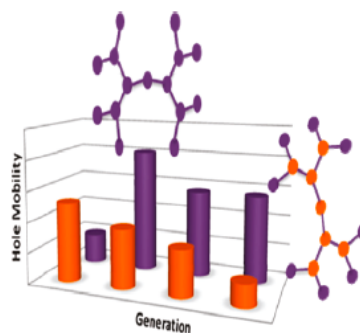
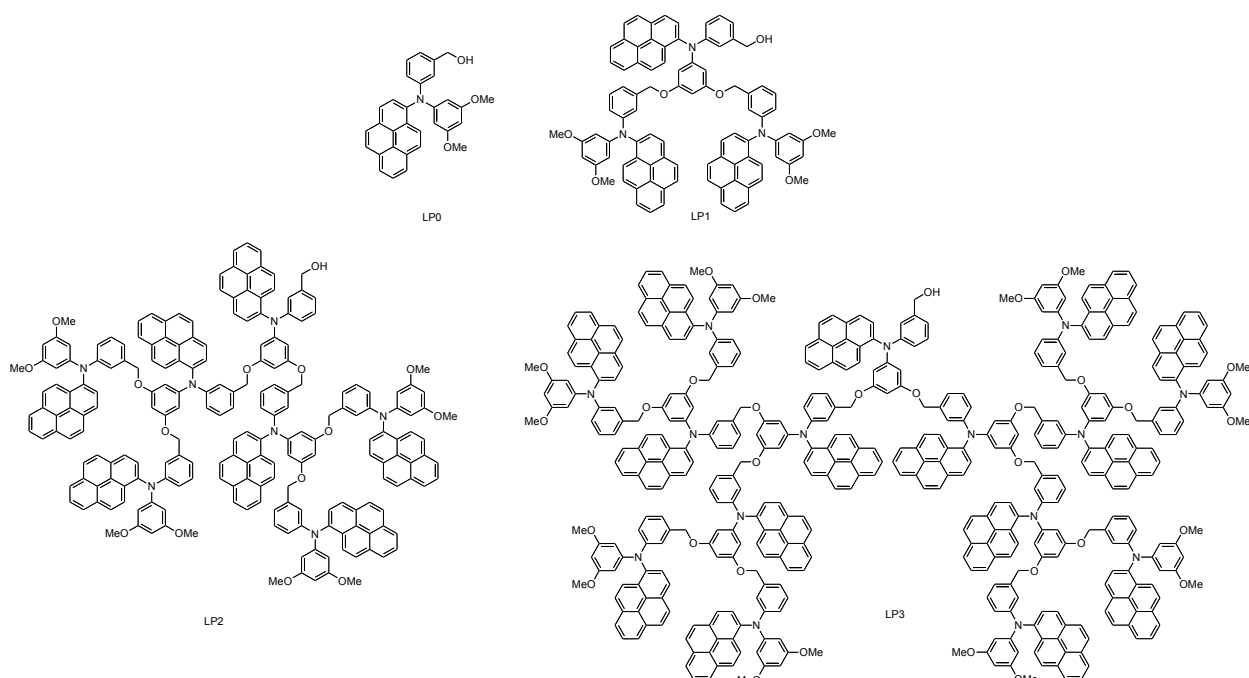
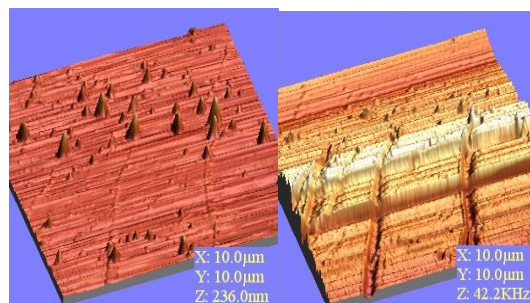


Figure 2. Schematic of the charge mobility trend in dendrons (purple units represent charge transport functionalities and orange units represent insulating moieties).

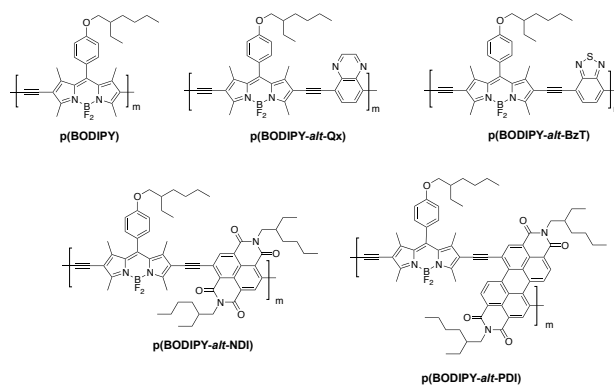


1.3. Barnes has completed some interesting proof-of-concept investigations with this instrument. Figure shows a topographical (AFM) scan of 50-nm (nominal) polythiophene nanoparticles and 2-dimensional polythiophene ‘fibrils’ – extended (and extremely fragile!) crystalline structures of a regio-regular polythiophene (P3HT). The crystalline structures are almost completely dark in terms of luminescence due to competition between charge separation and radiative recombination. We are currently working on dual-wavelength probes of these polythiophene systems where the ratio of absorbance strength at the two wavelengths (532 nm vs 630 nm) gives a quantitative measure of the crystalline to amorphous polymer averaged over the 75 nm diameter probe area. We anticipate a number of important experimental results to come from this instrumentation in the coming year.



(Left) AFM surface topology and (Right) near-field optical scan in absorbance mode of polythiophene nanoparticle/fibril sample. The dark regions in the near-field scan indicate regions of strong absorbance of the input light (attenuation of back-scattered signal).

1.4. 4,4-Difluoro-4-borata-3a-azonia-4a-aza-s-indacene dyes, more commonly known as BODIPY dyes, have been long since recognized for their excellent optical properties such as large absorption coefficients, high fluorescence quantum yields and remarkable photostability. Owing to large extinction coefficients, intense absorption spectra that extend into the red region



of the visible spectrum and decent hole-mobility, BODIPY derivatives are of great interest solar cell applications. π -conjugated polymers based on the BODIPY-core naturally extend the absorption into the deep-red regions of the visible spectrum and, in some cases, are excellent near-infrared emitters. The relatively high extinction coefficients of these polymers combined with their photostability make them attractive candidates for polymeric photovoltaics. Based on the prior knowledge that small molecule BODIPY derivatives function as electron donors in BHJ solar cells, it is reasonable to assume that the corresponding homopolymers involving the BODIPY core in the π -conjugated backbone should also function as donor polymers in polymer-PCBM BHJ solar cells.

Thayumanavan recently studied BODIPY-based donor-acceptor polymers for their photophysical and charge transport characteristics (co-supported by the DoE Energy Frontier Research Center on Polymer-Based Materials for Harvesting Solar Energy). The electrochemical characteristics of several small-molecule BODIPY derivatives show excellent reversibility during both oxidation and reduction. To us, this implies that the BODIPY core is capable of stabilizing an additional electron as well as a hole, both in small molecules and in π -conjugated polymers. Indeed, the cyclic voltammogram of our BODIPY-based homopolymer clearly indicates both reduction and oxidation behavior in thin films. This provides us with a unique and rare opportunity to systematically study the effect of different electron-rich or electron-poor comonomers on the optical and electrochemical properties of BODIPY-based conjugated alternating copolymers, which is currently lacking in literature. Amongst the myriad of acceptor units studied so far, *o*-quinoid acceptors such as 2,1,3-benzothiadiazole, quinoxaline, thieno[3,4-*b*]pyrazine, benzo[1,2-*c*,4,5-*c'*]bis[1,2,5]thiadiazole and [1,2,5]thiadiazolo[3,4-*g*]quinoxaline have garnered much attention. Alternating copolymers made from BODIPY donors and these *o*-quinoid acceptor heterocycles are highly polarized and possess small HOMO–LUMO gaps leading to absorption spectra extending into the near-infrared region.

1.5. Absorption of incident light is the preliminary process in the function of an organic photovoltaic (OPV) device. Needless to say, numerous materials, both small-molecules and polymers, have been designed and synthesized towards the end goal of maximizing light absorption in these materials. However, tuning light absorption (band gap) in conjugated polymers causes a simultaneous alteration in the frontier molecular orbital (FMO) energy levels, both HOMO & LUMO, thereby affecting the OPV device performance. To address this dichotomy, we chose to systematically investigate the influence of various “electron-rich”

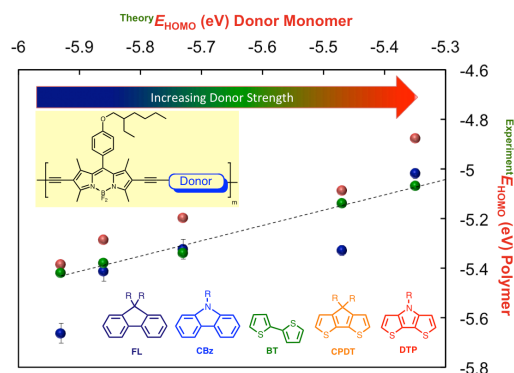
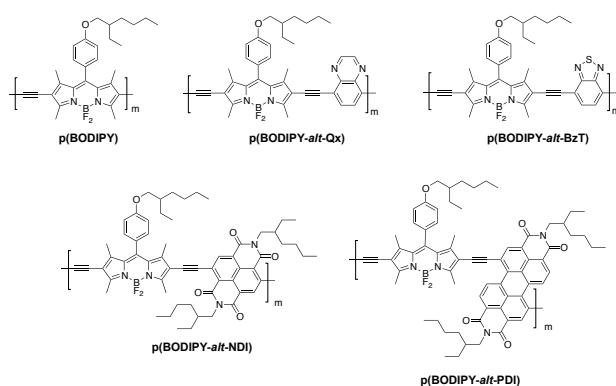


Figure 3. Correlation of experimentally determined HOMO energy levels (y-axis) of the polymers with theoretically calculated ones (x-axis)

donor units on the FMO energy levels of the corresponding BODIPY-based copolymers. These donors were chosen based on their calculated (DFT) gas-phase ionization potentials (IPs) as shown in the adjoining figure. Based on our calculations on ‘repeat units’ of these polymers, we found that while the HOMO was delocalized across the unit, the LUMO was centered on the BODIPY core. Thus, we hypothesized that the HOMO energy levels of the copolymers should depend on the IPs of the corresponding donor units while the LUMO energy levels should remain invariant. Indeed, as can be seen in the figure, the HOMO energy levels of the copolymers (determined experimentally) bear a linear correlation with the IPs of the donor units (calculated theoretically). Thus the copolymer p(BODIPY-*alt*-FL) possessed the lowest, while p(BODIPY-*alt*-DTP) possessed the highest HOMO energy level, respectively. These findings establish, for the first time, a much sought-after correlation between theory and experiment for rational design of conjugated polymers based on the BODIPY-core. Additionally, all polymers retain the broad and intense absorption characteristic of all BODIPY-based conjugated polymers, making them truly panchromatic. (*Chem. Sci.*, **2012**, 3, 3093-3102)

1.6. Extended π -structures have attracted significant attention from several fields, especially in organic electronics because, the intermolecular frontier molecular orbital overlap in condensed phase is thought to greatly influence charge transport in these materials. Thus, it is reasonable to assume that these desired MO overlaps will be enhanced in flat aromatic systems with a large π -surface area. Fused systems containing both thiophene and pyrrole units are interesting, because they have the potential to retain the advantages of both pyrrole (*N*- functionalization for solubility and packing) and thiophene units ($S\cdots S$ interactions in the condensed phase). With this in mind, we considered the thienopyrrole core as a promising unit to construct the extended fused structures (unsymmetric 7-member and symmetric 9-member, Figure 4).

The optical and electrochemical properties of these molecules were found to depend on the relative position of the nitrogen and sulfur atoms in the molecule (Figure 5). UV-vis absorption spectroscopy revealed that the 7-*syn* (1) isomer had better electron delocalization compared with 7-*anti* (2) as is evident from a much lower energy absorption onset for the former. Solution-state cyclic voltammograms recorded on these molecules reveal that the first oxidation potential for 7-*syn* is 180 mV more positive than 7-*syn* implying a better π -conjugation in the former. This is in accordance with the UV-vis absorption spectroscopy data. (*Org. Biomol. Chem.* **2012**, 10, 3455-3462).

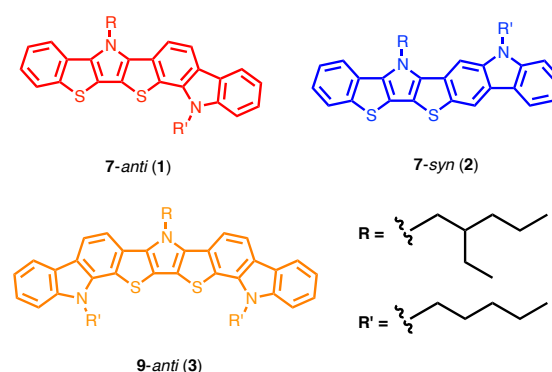


Figure 4. Chemical structures of the 7- and 9- member fused ring systems

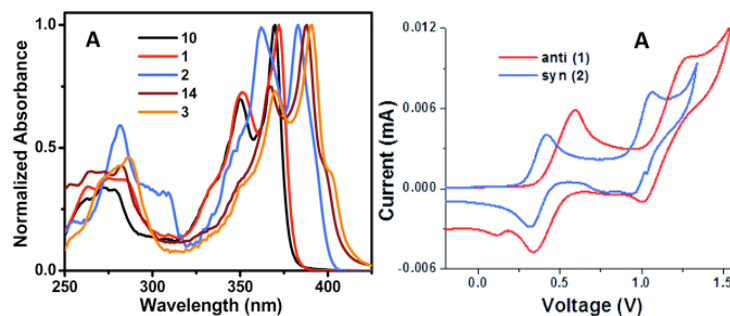


Figure 5. UV-vis absorption spectra and cyclic voltammograms for the fused systems

2. Materials for fuel cell applications

2.1. We have systematically studied the effect of charge carrier density and flexibility of the polymer containing 1*H*-1,2,3-triazole as a protogenic group on proton conductivity. 1*H*-1,2,3-triazole is expected to have higher proton conductivity compared to imidazole. 1,2,3-triazole is a liquid at room temperature, unlike imidazole, and is much more acidic than imidazole. In addition, 1,2,3-triazole has one more nitrogen atom in the ring than imidazole, leading to different tautomers of triazole and reduced conformational changes for proton conduction. Liu and coworkers reported the conductivity of poly(4-vinyl-1*H*-1,2,3-triazole) as being 10^5 times higher than that of poly(vinyl imidazole).^{1,2} The conductivity of imidazole-functionalized polysiloxanes has been reported to be 4 orders of magnitude more than that of poly(vinyl imidazole) due to the increased local mobility of the heterocycle in the former system. Previous work by the Coughlin and Tuominen groups³⁻⁵ has shown that the maximum conductivity with triazole-functionalized polysiloxanes is $10^{-3.5}$ S/cm, which is close to that reported by Liu and coworkers for poly(4-vinyl-1*H*-1,2,3-triazole). We expected a huge increase in the conductivity of triazole-functionalized polysiloxane as compared to poly(vinyl triazole), since we have seen that proton conductivity depends on the local mobility of the heterocycle within the polymer system, and that both imidazole and triazole conduct protons by means of Grotthuss-type mechanisms. We therefore undertook a detailed study of poly(vinyl triazole) that included investigations of proton transport on both the macroscopic and microscopic scales.

Coughlin synthesized poly (4-vinyl-1*H*-1,2,3-triazole) (PVTz) polymer and studied its anhydrous proton conducting properties, in order to examine the properties of both the polymer in the pristine state and polymers containing varying contents of residual solvent dimethyl formamide (DMF). Poly(4-vinyl-1*H*-1,2,3-triazole), having a minimum number of extra atoms other than heterocycle, provides us with an opportunity to study the proton dynamics on a microscopic scale of triazole tethered to a polymer using NMR, as there would be minimum influence of resonances of polymeric backbone under NMR. In the near future this project will look at microscopic proton dynamics of this system using solid-state NMR.

AC impedance data was obtained by Tuominen using a Solatron 1287 potentiostat/1252A frequency response analyzer. Measurements were done by pressing the material between two blocking electrodes, followed by application of 100 mV voltage with a frequency sweep from 3×10^5 to 1×10^{-1} Hz under vacuum to ensure an anhydrous environment. The resulting Z'' vs. Z' plot was used to determine the resistance values at the minimum imaginary response. Given the area and thickness of the membrane, conductivity can be calculated from the resistance measured. This “home-built” system for automated acquisition of impedance spectroscopy data for the purpose of proton conductivity measurements of new materials is being interfaced with an informatics software platform to enable data mining of proton conductivity and other data related to proton dynamics.

2.2. Proton transport, a fundamental chemical reaction is of core importance to many energy conversions and associated charge transport processes in chemical, biological and in technological applications. Proton transport across biological membranes is an essential process to life itself (respiration, metabolism) and, from a clean energy perspective, is a critical process in the operation of hydrogen fuel cells. To enhance the efficiency of proton transport across

membranes, especially at higher temperatures (operating temperature of fuel cells), there is a great interest in achieving proton transport without the assistance of solvent, *i.e.* water. The current polymer standard for proton transport, Nafion, fails at high temperatures. A viable pathway for achieving such anhydrous proton transport involves the Grotthuss mechanism.

N-Heterocyclic systems have been pursued as the potential candidates for proton transport. With the advent of click chemistry between azides and alkynes, triazoles have been pursued as the possible proton transport functionality. It has been shown in the literature that triazoles outperform imidazoles in proton conductivity. In order to fundamentally understand the reasons behind this behavior, Coughlin is studying proton conduction in the parent system poly(4-vinyl-1*H*-1,2,3-triazole), which is the simplest polymer containing triazole. Triazole resembles imidazole-pyrazole couple and has access to both *imidazole-like* and *pyrazole-like* pathways (Figure 6b). To understand the relative contributions of *imidazole-like* and *pyrazole-like* pathways toward the proton transfer in 1*H*-1,2,3-triazole systems, structurally analogous polymers based on *N*-heterocycles (triazole, imidazole and pyrazole) and benz-*N*-heterocycles (benzotriazole, benzimidazole, benzopyrazole) were synthesized modularly (Figure 6a) and their proton conductivities were evaluated (Figure 6c) by Thayumanavan and Tuominen. It has been found that triazole (benzotriazole) and imidazole (benzimidazole) containing polymers exhibit similar proton conductivities, about 4 orders of magnitude higher than those with pyrazole (benzopyrazole) (Figure 6b). The similar behavior of triazole and imidazole (benzotriazole and benzimidazole) polymers and the poor proton conducting ability of pyrazole (benzopyrazole)

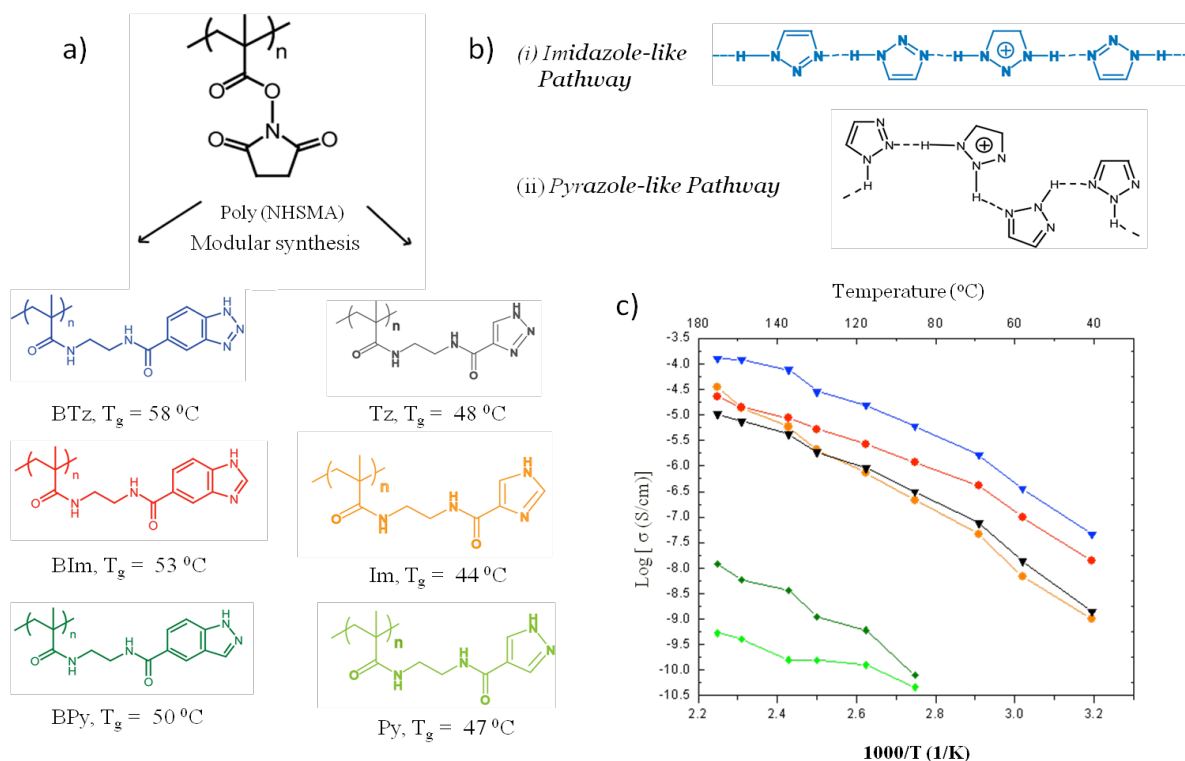


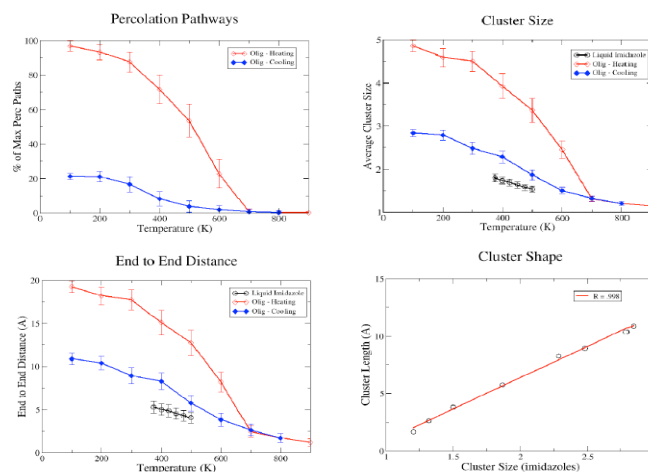
Figure 6. a) Structures of polymers based on benz-*N*-heterocycles (benzotriazole, benzimidazole, benzopyrazole) and *N*-heterocycles (triazole, imidazole and pyrazole); b) Proton conduction pathways in 1*H*-1,2,3-triazole; c) Proton conductivity of the polymers.

polymer has prompted us to conclude that the *imidazole-like* pathway is the significant contributor toward the proton transfer in 1*H*-1,2,3-triazole systems, while the contribution from *pyrazole-like* pathway is negligible.

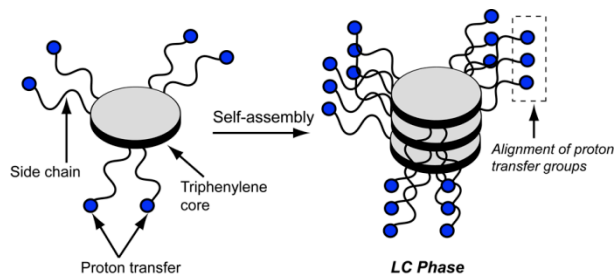
2.3. Designing proton exchange membrane (PEM) materials with tethered imidazoles that produce high conductivities has proven to be a formidable task. Grotthuss shuttling is highly dependent upon long range hydrogen bonding networks and without a fundamental understanding of these networks and its relationship to backbone architecture our design attempts will remain futile. Molecular dynamics simulations on imidazole containing oligomers have given us key insight into atomistic details that were otherwise inaccessible through experimental methods.

Imidazoles tethered to oligomeric aliphatic backbones have been modeled in the 100-900 K temperature range. Auberbach has shown that, while the system begins in a well-ordered state, it eventually becomes disordered at 700 K due to the breakage of hydrogen bonds. Cooling the system results in structural hysteresis which, ultimately, generates a plausible structure for comparison to experimental measurements. High level structural statistics including percolation pathways, cluster size, cluster length, and cluster shape have

been used to characterize the hydrogen bonding network. We have shown that by tethering imidazoles to oligomeric backbones we can produce more percolation pathways, longer clusters, and bigger clusters when compared to the liquid imidazole system. Additionally we can show that the clusters that form are relatively linear in nature. This is apparent when plotting the cluster length as a function of cluster size (Inset Figure). If this relationship is linear then we would expect the formation of linear clusters. If, instead, the relationship is sub-linear then we would expect to see the formation of bent clusters. The relationship that we see is the former. Linear clusters are more beneficial in PEMs as we would prefer the excess proton hops over a long distance and not necessarily across a large number of imidazoles.



With the theoretical studies above in hand, Venkatarman, Hayward, and Tuominen studied the liquid crystalline materials for proton transport, where triazole units are tethered. For efficient anhydrous proton transport, it is imperative that the proton conducting groups are organized into supramolecular structures that provide a continuous path for the proton. Moreover, the proton conducting groups should have sufficient flexibility for molecular reorientation to receive subsequent protons. We hypothesized that liquid crystalline (LC) phases may offer a balance between the



required supramolecular organization of the proton-conducting groups and the flexibility for molecular reorientation, thus providing a viable platform for developing efficient proton transporting materials (Inset Figure). We recently reported the synthesis, structure and performance of liquid crystalline (LC) proton conductors based on a triphenylene core with alkyl chains, whose termini are covalently attached to a triazole moiety. We showed that LC phase does lower the activation energy barrier for proton conduction by as much as 80%. We believe that LC materials are viable platforms for creating next generation PEMs. Further study to attach different proton transporting functional groups such as squaric acid and compare their proton conductivities are currently under investigation.

2.4. Proton transporting polymers that can selectively and efficiently transfer protons play a pivotal role in the overall operation of a hydrogen fuel cell. Polymers that can conduct protons under anhydrous conditions are particularly interesting for applications as proton exchange membranes in high temperature hydrogen fuel cells. We have recently introduced a new class of functional groups, phenols, for anhydrous PT and have shown that polymers based on phenols allow for facile reorientational dynamics. It has also been shown, with the help of theoretical modeling, that the pentamers of polystyrene (tri OH) (Fig. 7) can form extended intrachain hydrogen bond network. Both intrachain and interchain proton transfer events are important for long range PT. We hypothesized that a molecular architecture that presents PT moieties in orthogonal planes would be interesting as it would allow for greater interchain hydrogen bonding interactions along with intrachain interactions among PT moieties, thereby enhancing the overall PT.

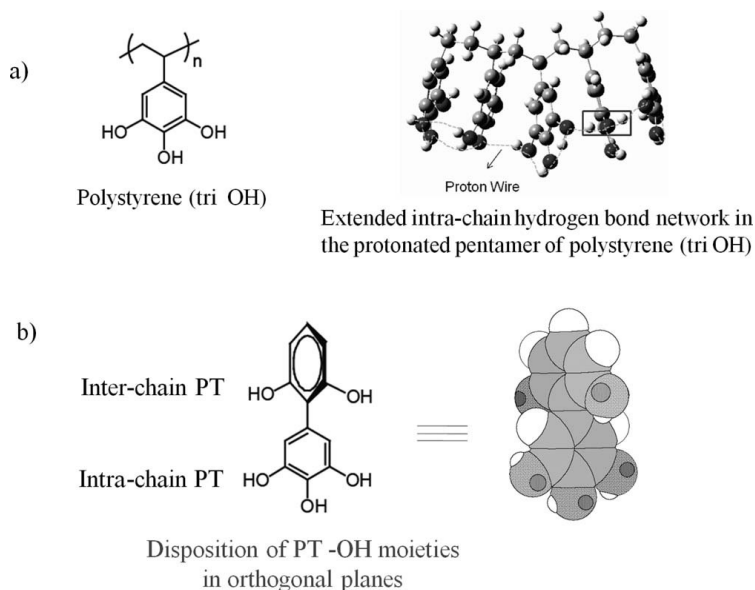
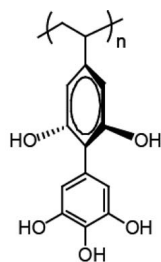


Figure 7. (a) Proton wire of polystyrene (tri OH) pentamer; (b) illustration of the spatial disposition of proton transporting -OH moieties in orthogonal planes.

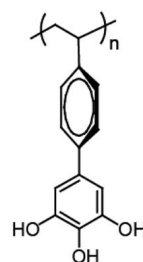
Table 1. Charge Carrier Density, Apparent Activation Energy (E_a), and Glass Transition Temperature (T_g) of Phenolic Polymers

Polymer	Weight Fraction of -OH Units	Log [σ (Scm ⁻¹)] at 140 °C	E_a /kJ mol ⁻¹
Polybiaryl (penta OH)	32	-6.4	77
Polybiaryl (tri OH)	22	-7.6	74
Polystyrene (tri OH)	33	-4.5	94

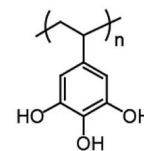
Biaryl hydroxy polymers with orthogonal disposition of proton transporting -OH moieties have been synthesized via conventional free radical polymerization. The polymers are characterized for their thermal stability and proton conductivity, and the results are compared with the corresponding styrenic hydroxy polymers (Chart 1). The biaryl architecture is observed to enhance



Polybiaryl (penta OH)



Polybiaryl (tri OH)



Polystyrene (tri OH)

Chart 1. Structures of biaryl and styrenic hydroxy polymers.

the thermal stability of phenol-based polymers. All polymers were found to be stable up to at least 220 °C both under nitrogen and air atmosphere. Incorporation of proton transporting -OH moieties on both phenyl rings of the biaryl scaffold increases the T_g of biaryl polymers. The orthogonal disposition of -OH moieties in biaryl polymers does result in lower E_a for proton transport (Table 1). However, this did not afford a net increase in the proton conductivity, compared with the styrenic polymers over the temperature range investigated here. This is attributed to the observed increase in T_g , since the normalized proton conductivity of polybiaryl (penta OH) is either comparable or slightly higher than the styrenic polymer (Fig 8).

From a practical materials perspective, the proton conductivities of the phenol-based polymers are lower than Nafion. However, phenols are indeed useful model systems for pK_a -independent design strategies for PT polymers. We are encouraged by the fact that the functional group placement strategy does provide lower activation energy.

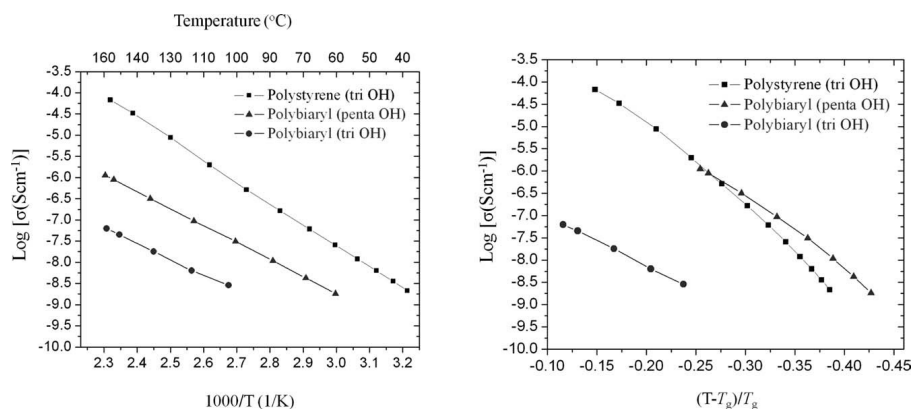


Figure 8. (a) Proton conductivity and (b) normalized proton conductivity of biaryl and styrenic polymers under anhydrous conditions.